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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
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By
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Determination of Chromium and Vanadium in Ores and Alloys after Oxidation with Perchloric Acid¹

Hobart H. Willard and R. C. Gibson

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

Chromium and vanadium may be completely oxidized to chromic and vanadic acid by boiling 70 per cent perchloric acid, the oxidizing action of which is removed by dilution with water, after which any of the usual titration methods may be used. Manganese is not oxidized.

Directions are given for applying this process to the analysis of chromic oxide, chromite, steel, and ferrochromium.

If phosphoric acid is added, manganese is oxidized more or less completely to a manganic salt, but the oxidation of chromium is hindered.

Small amounts of tungsten do not interfere but larger amounts must be removed before oxidation and may be subsequently added to the solution as sodium tungstate.

If both phosphotungstic acid and vanadium are present, low results are obtained.

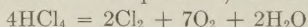
Chromium may be precipitated as lead chromate from a solution 1 molar in perchloric acid and 0.04 molar in lead perchlorate and thus separated from vanadium, manganese, and iron.

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MOST of the present volumetric methods for the determination of chromium depend upon its oxidation to chromic acid by an excess of oxidizing agent, removal of the latter, and titration with a suitable reducing agent. The removal of this excess of oxidizing agent and the effect of manganese are more or less troublesome. This paper describes a more rapid method for chromium in which the presence of manganese does not interfere.

About ten years ago one of the authors (11) reported that hot, concentrated perchloric acid would oxidize chromic oxide and its salts, and applied it to steel analysis, but the high price of the acid made its extensive use impracticable. The acid is now relatively inexpensive, and it seemed desirable, therefore, to study the method in detail so that it might find the wide use which its convenience and accuracy would seem to warrant. Up to the time this paper was presented (1), no further reference to this subject had appeared. Since that time Lichtin (6) has suggested the use of perchloric acid in the analysis of chrome alum and its liquors. He erroneously assumed that chloric acid was an intermediate product in the oxidation process. James (3) has given brief directions for its use in the analysis of chromium iron alloys. No analyses, however, were given to show the accuracy of his procedures, some of which are known to be inaccurate.

Perchloric acid, like sulfuric, in dilute solution is very stable and not affected by any of the ordinary reducing agents. Upon boiling it loses water until it reaches a concentration of 70 to 72 per cent, and this acid distills at about 203° C., accompanied by some decomposition, thus:



Oxides of chlorine are not formed.

This oxygen is available for oxidation and under these conditions the acid is a powerful oxidizing agent. To remove its oxidizing power, all that is required is dilution with water. The free chlorine present is readily removed by boiling or blowing air through the solution. Nearly all metals and non-metals are readily attacked by the hot, concentrated acid. Manganese, however, is not oxidized beyond the bivalent state except when considerable phosphoric acid is present. In this respect it differs from other oxidizing agents for chromium. Even chromite and chromic oxide, which are quite inert towards other acids, are completely oxidized. The method is very rapid. Moreover, since concentrated perchloric acid is an excellent dehydrating agent for silica (12), the latter may be determined after titration of the chromium with no extra trouble. It is not, however, satisfactory for removing tungstic acid (12).

In spite of the properties mentioned above, 70 to 72 per cent perchloric acid is perfectly stable and non-oxidizing at ordinary temperatures, but obviously should be kept out of contact with organic matter. It is non-explosive and no trouble

has been experienced with violent reactions, even when used by students.

Commercial perchloric acid, free from ammonium, chromium, and vanadium, is entirely satisfactory for the determination of the latter elements and is much cheaper than the C. P. acid.

Standardization of Dichromate

C. P. potassium dichromate, unless specially purified, is not a safe primary standard. It may even contain a slight excess of chromic acid. The material used in this work was the best obtainable, but it was tested in two ways—against U. S. Bureau of Standards arsenious oxide, which gave a value of 100.06 per cent dichromate, and against ferrous sulfate which had been titrated against permanganate standardized against Bureau of Standards sodium oxalate, which gave 100.16 per cent. The arsenite method (9) was more accurate because only one titration was involved and because dilution and acidity were without effect. The dichromate must not be added to the alkaline arsenite solution or too much arsenite will be used. One gram of dried potassium dichromate was dissolved in 25 cc. of water and acidified with 6 to 8 cc. of sulfuric acid (sp. gr. 1.5). To this solution was added 1.02 grams of dried arsenious oxide dissolved in 25 cc. of water and 3 grams of sodium hydroxide crystals. Reduction of dichromate was complete in a minute or two. Fifty cubic centimeters of hydrochloric acid (sp. gr. 1.1) were added and the excess arsenite titrated with 0.02 *N* bromate which had been standardized against arsenious oxide using approximately the same concentration of hydrochloric acid. Change in acidity, volume of solution, and concentration of substances have a negligible effect on the ratio of arsenite to dichromate, but a certain minimum concentration of hydrochloric acid must be present in the bromate titration, the end point of which may be determined electrometrically (17) or by the use of methyl orange indicator, if the color of the solution is not too deep. The excess of arsenite may also be titrated with permanganate, using a trace of iodine as catalyst, with or without erioglauine A as indicator (5).

Standardization of Ferrous Sulfate

It has been shown by Eppley and Vosburgh (1) that the result of a dichromate-ferrous sulfate titration is influenced by acidity, volume of solution, and concentration of dichromate. Their results show variations of more than 0.5 per cent when these factors are varied. The following experiments confirm their results: In solutions 3.4 molar with respect to sulfuric acid, 25 cc. of 0.1 *N* dichromate in a volume of 150 cc. required 25.43 cc. of ferrous sulfate when titrated electrometrically, and when the volume was doubled, 25.35 cc. Portions of 50 cc. with the same acidity

required, in volumes of 100 cc. and 600 cc., 50.96 cc. and 50.66 cc., respectively, of another ferrous sulfate solution. The presence of ferric or perchlorate ion has no effect on the location of the end point. It is obvious, therefore, that it is essential to standardize the ferrous sulfate under the same conditions of acidity and volume prevailing in the analysis, using preferably, about the same amount of titrating solution.

If it is desired to use diphenylbenzidine as indicator (15), the acidity must be reduced by the addition of sodium acetate sufficient to react with all free sulfuric or perchloric acid. This was shown by titrating 25-cc. portions of 0.1 *N* dichromate under different conditions. In all cases the solution had a volume of 150 cc. and contained 15 cc. of phosphoric acid (sp. gr. 1.37). In one case it was titrated directly, using diphenylbenzidine as indicator, and required 25.51 cc. of ferrous sulfate. In two parallel experiments the solution contained 20 cc. of 70 per cent perchloric acid, was treated with 32 grams of sodium acetate trihydrate, and the value, 25.41 cc., was obtained both electrometrically and by the indicator method.

To work out the conditions necessary to obtain satisfactory chromium determinations, synthetic mixtures of iron and chromium were prepared using ingot iron and the tested potassium dichromate. The oxidation was carried out in a beaker 20 cm. in height and of 350 cc. capacity. This extra-tall beaker, ordinarily unnecessary, was used to avoid any possible loss, either by spraying from the gases evolved or from the occasional bumping of the dilute perchloric acid. The concentrated acid boils quietly.

AMOUNT OF PERCHLORIC ACID REQUIRED—If too little acid was used, solid ferric perchlorate separated even in the boiling acid and the results were low. For 1 gram of iron, 20 cc. of 70 per cent acid were satisfactory, for 2 grams, 25 cc., and for 5 grams, 60 cc. Less is likely to cause incomplete oxidation of chromium, especially if the sample is dissolved directly in the hot acid, some of which is thus used up.

TIME OF BOILING FOR COMPLETE OXIDATION—The oxidation is the critical part of the process. After the acid has concentrated to dense fumes, 20 minutes of gentle boiling is sufficient, unless some reducing material, such as carbon, is present. Oxidation starts rather suddenly and the change in color due to the formation of red chromic acid is usually quite evident. Ten or fifteen minutes more is sufficient to complete the oxidation. The beaker must be kept covered, and should be at least 11 or 12 cm. high, the 500-cc. tall form with lip being satisfactory. A Soxhlet flask of this capacity is still better and prevents any possibility of mechanical loss by bumping or spraying. A conical flask is not so good because the depth of liquid is not great enough. Most of the acid condenses and runs down in oily drops on the sides of the vessel and on the cover glass. This appearance is an excellent sign that the acid is sufficiently concentrated

to have its maximum oxidizing power. Much time is saved by dissolving the sample directly in the concentrated acid, if possible, taking care not to heat too strongly at first. When the solution must be evaporated to fumes, especial care is needed to prevent mechanical loss.

If the concentrated acid solution is allowed to stand overnight before titration, some oxygen is apparently lost and results are slightly low.

TIME OF BOILING TO REMOVE CHLORINE—Three minutes was found sufficient. The solution must, of course, first be diluted to at least double its volume. The chlorine may also be removed by bubbling air through the solution.

INTERFERENCE OF AMMONIUM SALTS—Slightly low results were always obtained in the presence of ammonium salts. The error amounted to about 1 mg. of chromium in 50 mg. when 1 gram of ammonium nitrate was added. It is therefore important that when commercial perchloric acid is used, it be free from ammonium salts.

ACTION OF OTHER SUBSTANCES—Halides, nitrate, and acetate are volatilized. Sulfate in moderate amount does not interfere except that most sulfates are insoluble in perchloric acid and cause bumping. Reducing agents in general and even graphitic carbon are entirely oxidized in a short time. Vanadium is completely oxidized to vanadic acid. Tungsten in large amounts is incompletely oxidized by perchloric acid, and if already oxidized to tungstic acid, carries down appreciable amounts of chromium and vanadium. Phosphate in considerable amount, as will be shown later, tends to prevent complete oxidation of chromium unless the quantity of perchloric acid is greatly increased.

The results shown in Table I were obtained by the following procedure: The requisite amounts of ingot iron and potassium dichromate were weighed into a tall, 400-cc. lipped beaker. Five cubic centimeters of water and 1 cc. of nitric acid were added, and enough hydroxylamine hydrochloride to reduce the chromium. At least 25 cc. of 70 per cent perchloric acid were added, followed by the desired amount of ingot iron. The solution was boiled until the appearance of dense white fumes of perchloric acid and for 15 to 20 minutes longer to complete the oxidation. An equal volume of water was added to the somewhat cooled solution, which was boiled to expel chlorine, diluted, cooled, and titrated electrometrically with ferrous sulfate standardized at the time it was used, against dichromate under the same conditions of volume and acidity.

Procedure for Chromium and Vanadium Steels Containing Little or No Tungsten

Place samples of 0.5 to 2 grams, depending on the chromium content, in a 500-cc. tall-form lipped beaker, or better still in a 500-cc. Soxhlet flask, and add 20 to 25 cc. (depending on the size of the sample) of 70 per cent perchloric acid,

commercial or c. p. Cover the vessel and warm until all the metal has dissolved, taking care not to let the action become too violent. Most steels will dissolve in less than 5 minutes. Boil the solution 15 to 20 minutes, noting the change in color if much chromium is present, and continuing the boiling at least 10 minutes longer. The perchloric acid should condense and run down the sides of the beaker or flask. Cool somewhat, add an equal volume of water, and boil 3 minutes to expel chlorine. After cooling, the solution is diluted to a suitable volume and is ready for titration as described later.

Table I—Determination of Chromium and Vanadium in Synthetic Mixtures of Iron and Chromium after Oxidation with Perchloric Acid

WEIGHT OF SAMPLE Grams	CHROMIUM ADDED %	CHROMIUM FOUND %
5	0.274	0.273
5	0.264	0.263
2	0.708	0.707
2	0.666	0.664
1.5	0.879	0.876
1.5	1.020	1.020
0.4	14.23	14.21
0.4	14.48	14.48
0.35	77.47	77.43
0.35	76.53	76.52

Cast iron or alloys high in carbon should be dissolved in dilute perchloric acid, either with or without nitric acid, and evaporated to fumes; the action of the hot concentrated acid is too violent. If it is necessary to use 4- or 5-gram samples, add 50 or 60 cc. of acid. This is desirable in cast iron or steel very low in chromium. Boiling for 1 or 2 hours may be necessary to oxidize all the graphite, and further addition of perchloric acid may become necessary.

Procedure for Ferrochromium

An alloy of this type requires different treatment, because when boiled with 70 per cent perchloric acid, the chromium trioxide formed, which is fairly insoluble even in the hot acid, tends to coat the particles of ferrochromium and prevent further oxidation. Weigh 0.2 gram of the powdered alloy into a 500-cc. tall lipped beaker or Soxhlet flask. Add 20 cc. of hydrochloric acid, sp. gr. 1.18, and heat for 15 minutes. Add 15 cc. of 70 per cent perchloric acid and boil 30 minutes after all hydrochloric acid is expelled. Cool somewhat, add a few cubic centimeters of water to dissolve the chromium trioxide, and reoxidize by boiling 15 minutes after the water is expelled. Add a few cubic centimeters of water and look for any undissolved particles of metal. If any are present, another oxidation may dissolve them. Otherwise pour off most of the solution, add a few cubic centimeters of 70 per cent perchloric acid to the residue, and boil till solution is complete. Add the main decanted liquid, evaporate off the water, and reoxidize for 5 minutes. Dilute and boil off chlorine.

Table II shows the results obtained with steels and ferrochromium.

Table II—Determination of Chromium and Vanadium in Steel and Ferrochromium after Oxidation with Perchloric Acid

WT. OF SAMPLE	CHROMIUM PRESENT	CHROMIUM FeSO ₄ indicator	FOUND FeSO ₄ electro- metric	ARSENITE	VANADIUM PRESENT	VANADIUM FOUND(6)
				PERMAN- GANATE(5)		
Grams	%	%	%		%	%
Cast Iron, B. S. 82						
5	0.24	0.240	0.240			
5	0.24	0.239	0.240			
5	0.24	0.240				
Cr-Ni Steel, B. S. 32b						
2	0.638	0.637	0.637			
2	0.638	0.636	0.638			
Cr-Mo Steel, B. S. 72						
1.5	0.911	0.908	0.909			
1.5	0.911	0.910	0.909			
Stainless Steel, B. S. 73						
0.4	13.93	13.89	13.90	13.88		
0.4	13.93	13.92	13.89	13.88		
0.4	13.93	13.92	13.91			
Ferrochromium, B. S. 64						
0.15	67.9	67.80	67.78			
	67.9	67.79	67.81			
Cr-V Steel, B. S. 30a						
2.0	1.02			1.005	0.21	0.21
2.0	1.02			1.010	0.21	0.21
2.0	1.02			1.010	0.21	0.21

Procedure for Chromic Oxide and Chromite

Chromic oxide, which is not attacked by the usual acids, is readily oxidized to chromic acid by boiling 70 per cent perchloric acid, a 0.15-gram sample requiring 15 minutes. Chromite is more resistant; if ground to pass a 200-mesh sieve it requires 60–90 minutes. Storer (7, 10) suggested the use of concentrated nitric acid and sodium chlorate for this purpose. Gröger (2) used it successfully for chromic oxide, but both he and others found that it did not completely dissolve chromite.

Pure chromic oxide was prepared by precipitating mercurous chromate from chromic acid solution and igniting it in hydrogen.

Weigh a 0.5-gram sample into a tall, 500-cc. lipped beaker, or better still, Soxhlet flask. Add 20 cc. of 70 per cent perchloric acid and boil 30 to 60 minutes. Cool somewhat, then add a few cubic centimeters of water to dissolve the chromium trioxide which coats the particles. If any unattacked ore remains, evaporate off the water and boil the concentrated acid again for 20 or 30 minutes. If this treatment does not decompose all the ore, pour off most of the solution, add to the residue 10 cc. of perchloric acid, and boil until the ore is dissolved. Add the main decanted solution, evaporate off the water, oxidize 5 minutes, dilute, and boil off the chlorine. The solution is diluted to a suitable volume and when cool, is ready for titration.

The results obtained by this procedure, using samples of chromite and pure chromic oxide, are shown in Table III.

Table III—Determination of Chromium in Chromic Oxide and Chromite after Oxidation with Perchloric Acid

CHROMIC OXIDE PRESENT		CHROMIC OXIDE FOUND (Electrometric)
Gram		Gram
0.1423	CHROMIC OXIDE	0.1424
0.1401		0.1401
0.1409		0.1408
0.1423		0.1422
0.1471		0.1471
	CHROMITE	
%		%
57.49 ^a		57.48
57.49		57.47

^a Decomposed by perchloric acid, oxidized by persulfate.

Titration of Chromic Acid

After the chromium has been oxidized as already described, it may be titrated by any of the usual methods.

(1) Excess of standard ferrous sulfate is added and the excess is titrated back by means of standard permanganate, allowing 1 minute for the end point if vanadium is present. This method is so well known as to need no description. The color due to ferric perchlorate is so slight that there is no advantage in adding phosphoric acid. In the absence of vanadium, the end point is made much sharper by adding 0.5 cc. of a 0.1 per cent solution of erioglaucine A, better known as alphazurine (Schultz 506) as recommended by Knop (4). The change from green to red after the addition of an excess of 0.03 cc. of 0.1 *N* permanganate in 300 cc. is very distinct even in the presence of the chromic salt. The color lasts only a few seconds.

(2) Excess of standard arsenite is added, which is then back-titrated with permanganate in the presence of hydrochloric acid and a trace of iodide as catalyst, as described by Kolthoff and Sandell (5). If vanadium is absent, alphazurine as indicator improves the end point. In testing this method 2-gram samples were used, phosphoric acid was not really necessary, and vanadium was determined in the same solution by titration with ferrous sulfate using diphenylbenzidine as indicator, following the directions of the authors. Good results were obtained. The amount of acetate to be added is discussed in connection with the next method.

(3) The chromic acid (and vanadic acid, too, if present) is titrated directly with standard ferrous sulfate either electrometrically in a strongly acid solution, or by the use of diphenylbenzidine as indicator in a solution containing phosphoric acid and sufficient sodium acetate to react with all the perchloric acid present according to the method of Willard and Young (15). The procedure is as follows: After boiling off the chlorine, cool, dilute the perchloric acid solution to 200 to 400 cc., add 15 cc. of phosphoric acid (sp. gr. 1.37) and, stirring constantly, a weight of sodium acetate trihydrate equivalent to the excess of perchloric acid used in dissolving the steel. One gram of iron was

found to require about 5.4 cc. of 70 per cent perchloric acid for conversion into ferric perchlorate, and 1 cc. of this acid contains 1.17 grams of perchloric acid, equivalent to 1.58 grams of crystallized sodium acetate. Thus, if 20 cc. of acid are added, the excess will require about 23 grams of acetate. If the steel was first dissolved in nitric acid, the excess of perchloric acid will be a little greater. The proper amount of acetate has been added when more would form a permanent white precipitate of ferric phosphate. If this occurs, add dilute sulfuric acid, with constant stirring, until the solution clears. Unless the acidity is reduced in this way, the color change at the end point will be slow. Add 0.6 to 0.8 cc. of 0.1 per cent diphenylbenzidine solution (in phosphoric or acetic acid), and allow 5 minutes, but not more than 10, for the purple color to develop. It will appear brownish until most of the chromic acid is reduced. If no color appears, add a few drops of dilute sulfuric acid. Titrate with ferrous sulfate to a clear green, approaching the end point carefully. Add a correction of 0.04 cc. of 0.1 N ferrous sulfate for each 0.5 cc. of indicator.

For the electrometric method add 25 to 30 cc. of sulfuric acid (sp. gr. 1.5) and titrate chromic plus vanadic acids with ferrous sulfate. If much vanadium is present, a much sharper end point is obtained by cooling the solution to 5° C.

Whichever method is used, it has already been shown that the ferrous sulfate should be standardized in the same way and under the same conditions of volume and acidity at about the time it is used.

Titration of Vanadium

This may be determined by any of the usual methods, a list of which is given in references (15) and (5).

Silica has been dehydrated by the boiling perchloric acid and after the titration it may be filtered off and determined (12).

These different methods were used in obtaining the concordant results shown in Table II.

Steels Containing Tungsten

When present in considerable amount, tungsten is only slowly and incompletely oxidized by hot 70 per cent perchloric acid. The tungstic acid formed seems to protect some of the metal. Dilute acid dissolves the steel, leaving tungsten powder, which is incompletely oxidized by the concentrated acid. The steel was, therefore, dissolved in hydrochloric acid, the tungsten oxidized by boiling with nitric acid in the usual way, and the solution evaporated with 25 cc. of 70 per cent perchloric acid. The concentrated acid was boiled 20 minutes to oxidize the chromium which was titrated with ferrous sulfate. The steel contained 4.10 per cent chromium, 14.80 per cent tungsten, and no vanadium. The amount of chromium found was about 1 mg. too low.

The precipitate of tungstic acid was filtered off and dis-

solved in hot, dilute sodium hydroxide. It contained about 1 mg. of chromium, mostly as chromate, and accounted completely for the low results. The chromic acid is noticeably adsorbed by it. The precipitate takes on a deeper orange color. This effect was further shown by mixing sodium tungstate and chromate solutions, adding perchloric acid, evaporating, and boiling. The amount of chromium in the precipitate was always 1 or 2 mg. When vanadium was present, about the same proportion of it was found in the tungstic acid. Several days' leaching of the precipitate with dilute sulfuric acid failed to remove any of these metals. Moreover, the amount of ferric oxide in the precipitate was much greater. One-gram samples of Bureau of Standards Steel 50 containing 17.56 per cent tungsten, 3.61 per cent chromium, and 0.76 per cent vanadium, were treated as above. The precipitate of tungstic acid contained 6.4 mg. of iron, 1.4 mg. of chromium, and 0.3 mg. of vanadium as oxides. When corrected for these impurities, 17.63 per cent of tungsten was obtained. In a steel containing 5.8 per cent of tungsten it was difficult to obtain a clear filtrate, but even with cinchonine the value obtained was only 5.60 per cent. The procedure recommended by James (3) is, therefore, unsatisfactory. All the silica was contained in these precipitates.

It seemed worth while to try to prevent the interference of tungsten by converting it into the soluble phosphotungstic acid. Certain difficulties were encountered, however. Phosphoric acid tends to prevent complete oxidation of chromium by perchloric acid, as shown in Table IV. Dichromate was added and reduced by hydroxylamine hydrochloride. Each result is the average of two or more experiments.

Table IV—Effect of Phosphoric Acid on Oxidation of Chromium by Perchloric Acid

EIGHTY-FIVE PER CENT PHOS- PHORIC ACID Cc.	SEVENTY PER CENT PER- CHLORIC ACID Cc.	TIME OF OXIDATION Minutes	CHROMIUM PRESENT Mg.	ERROR CHROMIUM Mg.
5	20	15	100	-4
5	20	30	100	-7
15	20	15	100	-40
15	20	30	100	-50
5	25	20	50	-1.3
5	30	20	50	-1.0
5	35	20	50	-0.8
5	25	20	25	-0.5
5	32	25	25	-0.3
5	40	25	25	-0.3
5	30	25	25	-0.2
5	35	25	25	-0.1

Effect of Manganese

It is well known that trivalent manganese is stabilized by phosphoric acid. It was found that by boiling the correct mixture of perchloric and phosphoric acids, manganese could be quantitatively oxidized to a manganic salt and titrated by ferrous sulfate. If, therefore, chromium is oxidized in the presence of considerable phosphoric acid as described above, the manganic salt must be reduced before

the chromic acid is titrated, and dilute hydrochloric acid is suitable for this purpose. One-gram samples of steel to which manganese sulfate was added were boiled 25 minutes with 3 cc. of 85 per cent phosphoric acid and 35 cc. of 70 per cent perchloric acid. The solutions were diluted to 150 cc., the stated amounts of 2.3 *N* hydrochloric acid (one part of concentrated acid and four of water) added, and after boiling 5 minutes any manganic salt present was titrated electrometrically with ferrous sulfate. The results are shown in Table V.

Table V—Effect of Hydrochloric Acid (2.3 *N*) on Manganic Phosphate

MANGANESE PRESENT	MANGANESE FOUND AFTER ADDITION OF HCl					
	0	1 cc.	2 cc.	3 cc.	5 cc.	10 cc.
Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
11.3	5.1	3.3	1.0	0	0	0
51	18.0				0.3	0
101	40.6					0.2

In all cases there was insufficient phosphoric acid for complete oxidation. Ten cubic centimeters of 2.3 *N* hydrochloric acid are sufficient to reduce considerable amounts of manganese, and it was found that it would not reduce any of the chromium when 50 mg. of it and 2 grams of iron were present. Even 25 cc. caused only a slight reduction.

These results show that if even 5 cc. of 85 per cent phosphoric acid are present, the amount of perchloric acid must be greatly increased even with small amounts of chromium, and that with larger amounts, even this does not entirely eliminate the error.

It was found that 10 cc. of 85 per cent phosphoric acid were required to keep in solution 0.2 gram of tungsten when boiled with 30 cc. of perchloric acid. With 5 cc., a heavy cream-colored precipitate formed which persisted on dilution, but this amount of phosphoric acid was sufficient for 0.1 gram of tungsten, the slight precipitate dissolving on dilution. Three cubic centimeters were sufficient for 0.05 gram. In the presence of 1 and 2 grams of iron, however, 5 cc. are sufficient for 0.1 and 0.15 gram of tungsten, respectively. Using 3 cc. of phosphoric acid under the same conditions, a precipitate forms but dissolves when 10 cc. more are added after dilution, and the solution boiled. Table VI shows the results obtained by oxidizing the chromium under varying conditions, using in all cases 3 cc. of 85 per cent phosphoric acid and 35 cc. of 70 per cent perchloric acid. After dilution, 10 cc. more of the former were added. Each of the errors shown is the average of several experiments.

By using the conditions of the last experiment in Table VI, adding extra iron, dissolving the steel in a mixture of phosphoric, nitric, and hydrochloric acids, and reducing the manganic salt by hydrochloric acid, the right value was obtained for a steel containing 18.7 per cent tungsten and 3.13 per cent chromium. In another experiment using the conditions of the next to the last analysis in Table VI, the result was 3.08 per cent. This error of 0.5 mg. of chromium persisted

in all cases where 10 cc. of phosphoric and of dilute hydrochloric acid were added after the oxidation, and was probably due to some reducing material in the acid. One gram of steel containing 15 per cent of tungsten required no extra phosphoric acid to keep it in solution.

Table VI—Effect of Phosphotungstic Acid on Oxidation of Chromium by Perchloric Acid

IRON	TUNGSTEN	CHROMIUM	ERROR
Grams	Grams	Mg.	CHROMIUM Mg.
1	0.1	12	-0.07
1	0.1	50	-0.20
1	0.2	50	-0.25
2	0.2	50	-0.07
0.75	0.2	50	-0.35
2 ^a	0.2	50	+0.03

^a No phosphoric acid added after oxidation. Solution cleared on dilution.

Effect of Vanadium

If vanadium is present, low results for chromium are always obtained, so that the above method is of somewhat limited applicability. In the presence of phosphotungstic acid, Willard and Young (15) have shown that vanadic acid forms a complex which is only partially reduced by ferrous sulfate. Attempts to break up this complex by boiling with perchloric acid or by adding fluoride were without effect.

To show the magnitude of this error, varying amounts of vanadium as sodium vanadate were added to 1 gram of a steel containing 4.10 per cent chromium, which was treated as described above for chrome-tungsten steel. Assuming that all the chromium was titrated, the errors in vanadium, with 2, 10, and 30 mg. of the latter present, and 0.2 gram of tungsten, were -1.7, -3.9, and -5.0 mg., respectively. With 0.1 gram of tungsten, the corresponding errors were -1.5, -2.1, and -3.6 mg. of vanadium.

Method Not Involving Phosphoric Acid

Willard and Young (15) have shown that a large amount of tungstic acid, as sodium tungstate, may be added without precipitation to an acid solution containing sufficient ferric salt. This dissolved tungstic acid does not interfere in the electrometric titration of chromic and vanadic acids. In applying this to a chrome-vanadium-tungsten steel, from which tungsten had been removed in the usual way and the chromium and vanadium in the filtrate oxidized by perchloric acid, it was noticed that if the tungstic acid was dissolved off the filter by hot 4 per cent sodium hydroxide and added to the oxidized filtrate containing sufficient iron, the results were always low by 0.5 mg. of chromium, even if the tungstate solution had been oxidized by peroxide or persulfate. This was proved to be due to organic matter introduced by the filter paper, no matter whether the sodium hydroxide was hot, cold, or fairly dilute. Sodium carbonate solution did not cause this error but it was impossible to

oxidize all the chromium in the residue. It seemed essential, therefore, to fuse the tungstic oxide with sodium carbonate, the air acting as oxidizing agent. Although more troublesome, this method has been shown to eliminate all errors.

Procedure for Chromium or Chromium and Vanadium in Tungsten Steels

A sample of 1 to 1.5 gram is usually convenient. Place it in a 150- or 250-cc. beaker, and add 10 cc. of water and 30 cc. of hydrochloric acid (sp. gr. 1.18). Heat until the steel is completely decomposed and to the hot solution add cautiously from a pipet 8 to 10 cc. of nitric acid (sp. gr. 1.42), without removing the cover glass. Boil gently with occasional swirling until all dark metallic particles have been oxidized to yellow tungstic acid, and evaporate to 20 cc. If necessary, add 10 cc. of hydrochloric acid and 3 cc. of nitric, and boil down again to 20 cc. Dilute to 75 cc., boil a few minutes to dissolve all salts, filter into a 500-cc. Soxhlet flask, or, less satisfactorily, into a tall 500-cc. lipped beaker, and wash with hot, 2 per cent hydrochloric acid. Remove the flask or beaker and wash out the acid with 1 per cent ammonium nitrate solution, taking care that these washings are discarded because ammonium salts prevent complete oxidation of chromium.

To the filtrate add 1 gram of iron as ferric chloride or nitrate, but not sulfate; if a 1.5-gram sample was used, add only 0.5 gram of iron. Add 25 cc. of 70 per cent perchloric acid (or more if a larger sample was taken) and evaporate to fumes of the acid.

In the meantime, ignite the tungstic acid precipitate in an open platinum or iron crucible and fuse it for 5 minutes with 1.5 grams of sodium carbonate with free access of air. Or fuse with sodium peroxide in an iron crucible free from chromium, dissolve in water, and boil to remove peroxide.

Boil the main perchloric acid solution in the covered flask or beaker 20 minutes after the appearance of dense fumes of the acid. Dilute with an equal volume of water, boil 3 minutes to expel chlorine, and while still hot, pour into it with constant stirring the sodium tungstate solution together with the small amount of ferric oxide which it contains. A clear solution will result.

Determination of Chromium

If only chromium is to be determined, add to the cool solution excess of standard ferrous sulfate and titrate back with permanganate as previously described. No phosphoric acid is needed. The arsenite method of Kolthoff and Sandell may also be used. The ferrous sulfate must be standardized under the same conditions of acidity and volume.

Determination of Vanadium

Vanadium may be determined in the same solution after destroying the excess of permanganate by a drop of arsenite

(5), but the vanadic acid must be titrated electrometrically with ferrous sulfate, because, as has already been pointed out, tungsten prevents the formation of color with diphenylbenzidine.

The excess of permanganate may be conveniently destroyed by adding 1 or 2 cc. of 0.1 *M* sodium azide (16) and boiling for a moment, or at room temperature by adding more azide and letting stand a short time.

Boiling with a little dilute hydrochloric acid is also effective.

Determination of Chromium and Vanadium

To the perchloric acid solution, add 25 cc. of sulfuric acid (sp. gr. 1.5), cool, and titrate chromic and vanadic acids electrometrically with ferrous sulfate. If much vanadium is present, cool the solution to 5° C.

The tungstic acid in solution begins to precipitate after several hours.

Indicator Method for Chromium and Vanadium

This differs from the method just described in the removal of tungstic acid to prevent its interference with the indicator. Proceed as already described including the filtration and washing of the tungstic acid precipitate. Use paper pulp. The oxidation of chromium in the filtrate is carried out in the same way, except that no iron is added, and the titration is carried out as directed. If no color develops, it is probable that tungstic acid was not completely removed or too much acetate was added.

The small amounts of chromium and vanadium in the tungstic acid are determined colorimetrically after fusion in an open crucible with 1 or 2 grams of sodium carbonate (15). The melt is dissolved in water and filtered. If it is colorless, no chromium is present. If it is yellow, estimate the chromium by matching the color in a beaker with an alkaline solution of equal volume to which standard dichromate is added. Then acidify the solution with phosphoric acid and estimate the vanadium colorimetrically by the method of Willard and Young. If chromium is present, add to the vanadium standard an equivalent amount of dichromate.

One-gram samples of Bureau of Standards Steel 50 containing 17.56 per cent tungsten, 3.61 per cent chromium, and 0.756 per cent vanadium, were treated as described, the chromium being titrated by the ferrous sulfate-permanganate method, without any indicator. The values obtained were 3.61, 3.61, 3.60, 3.62, and 3.60 per cent. In the first experiment, 10 cc. of 85 per cent phosphoric acid were added before the permanganate titration, but the end point was sharper without it. The value for vanadium in one sample was found to be 0.753 per cent by adding 20 cc. of 0.1 *M* sodium azide to reduce the excess of permanganate,

letting stand 20 minutes at room temperature, and titrating vanadic acid electrometrically with ferrous sulfate.

It should be noted that perchloric acid is an excellent solvent for many alloys which dissolve with difficulty in other acids.

Separation of Chromium as Lead Chromate from Perchloric Acid Solution

It has been shown by Willard and Kassner (8, 14) that lead chromate is completely insoluble in 1 *M* perchloric acid which is 0.01 *M* in lead perchlorate, and practically insoluble in 5 *M* acid if twice as much lead is present. It would thus appear quite feasible to separate chromium from vanadium, manganese, and other metals by precipitation as lead chromate after oxidation by perchloric acid as described above. The results of experiments along this line showed that such a method was possible if proper conditions were maintained.

Lead perchlorate was prepared by evaporating lead nitrate with a slight excess of perchloric acid as described by Willard and Kassner (13), but no attempt was made to free it from acid. A salt prepared from litharge seemed to contain some reducing material. The solution was diluted to 0.5 molar.

Lead chromate was completely precipitated in a short time from a solution containing considerable iron, 1 *M* perchloric acid and 0.04 *M* lead perchlorate. These were adopted as standard conditions. Such a solution contains in 200 cc., 16 cc. of 0.5 *M* lead solution and 17 cc. of 70 per cent perchloric acid. Extra lead must be added if much chromium is precipitated, 100 mg. of chromium requiring 4 cc. of 0.5 *M* solution.

A solution oxidized by boiling perchloric acid always contains, after dilution, small amounts of chloride which interfere slightly with complete precipitation of lead chromate. The addition of a few drops of silver perchlorate, prepared from the nitrate in the same way as the lead salt, removed this source of error. It was sometimes necessary to neutralize part of the free acid, and ammonia was found best for this purpose because sodium hydroxide usually contains chloride and sometimes reducing substances. The procedure followed, after the perchloric acid solution had been boiled to remove chlorine, was to neutralize part of the acid if necessary, add a slight excess of silver perchlorate, heat just to boiling, add the proper amount of lead perchlorate, and cool to room temperature, stirring occasionally. If filtered hot, some chromate remained in solution. The precipitate was very dense and crystalline. It was filtered on a Gooch crucible, washed with cold water, transferred to a beaker, excess of standard arsenite added, then 50 cc. of hydrochloric acid (sp. gr. 1.09), after which the excess of arsenite was titrated with bromate. The lead chromate could also be dissolved in saturated sodium chloride solution containing 1 cc. of concentrated hydro-

chloric acid per 100 cc., and titrated with ferrous sulfate. If 1 gram of the steel is dissolved in 20 cc. of 70 per cent perchloric acid and diluted to 175 or 200 cc., the acidity will be about right.

Good results were obtained when about 80 mg. of chromium were present, but with 30 mg. there was an error of -0.2 to 0.3 mg., the cause of which is yet unexplained. Vanadium was determined in the filtrate by titration with ferrous perchlorate to avoid precipitation of lead sulfate, and the results were good when all the chromium had been precipitated. In a solution containing tungstic acid held in solution by ferric perchlorate, 0.6 to 0.8 mg. of chromium remained in solution. Further work is in progress to obviate the difficulties mentioned. Table VII shows the results obtained under proper conditions.

Table VII—Separation of Chromium as Lead Chromate

WEIGHT OF SAMPLE	CHROMIUM PRESENT	CHROMIUM FOUND	VANADIUM PRESENT	VANADIUM FOUND
Grams	%	%	Mg.	Mg.
Cr-Ni Steel, B. S. 32b				
2.2	0.638	0.635		
2.2	0.638	0.630		
Stainless Steel, B. S. 73				
0.6	13.93	13.89		
0.6	13.93	13.88		
Synthetic Mixture				
Grams Fe	Mg.	Mg.		
3	83.15	83.15	32.7	32.5
3	83.55	83.60	32.7	32.5

Manganese can be determined in the filtrate from lead chromate by methods not applicable in presence of chromium.

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Action of Perchloric Acid on Elements

Various metals in the form of foil 1 cm.² in area were boiled in 2 *N* perchloric acid until the metal had completely dissolved. Any chloride in the resulting solutions was determined as silver chloride. Only iron, cobalt and nickel formed considerable chloride, and these values are shown in the following table:

Formation of Chloride

METAL	WT. OF METAL Dis- SOLVED	TIME FOR SOLU- TION	WT. OF CHLORIDE	MILLI- ATOMIC WTS. OF CHLORIDE FORMED	ATOMIC WTS. OF METAL DISSOLVED	ATOMIC WTS. OF CHLORIDE FORMED FOR ONE ATOMIC WT. OF METAL
	<i>g</i>	<i>hrs.</i>	<i>g.</i>			
Fe	0.3277	4	0.0084	0.237	0.00587	0.0403
	0.3065	4	0.0073	0.206	0.00549	0.0375
Co	0.2959	12	0.0088	0.250	0.00502	0.0497
	0.3370	12	0.0101	0.285	0.00572	0.0499
Ni	0.3026	24	0.0009	0.024	0.00516	0.0047
	0.3066	24	0.0007	0.021	0.00522	0.0040

The action of nickel is seen to be quite different from that of cobalt and iron.

The process was further investigated as follows:

A metal forming only a trace of chloride when dissolved in perchloric acid was dissolved in 2 *N* perchloric acid containing ferric perchlorate or cobalt perchlorate. No appreciable amount of chloride was formed.

Two normal perchloric acid was electrolyzed using an iron or cobalt cathode and a platinum anode, varying the current density through a wide range, but again no chloride was formed.

Action on Selenium and Tellurium

The oxidation of these elements to selenic and telluric acids by boiling 70% perchloric acid is slow, only 75 to 85% being oxidized after 5 hours. If about 0.5 mg. of chromium is present to act as a catalyst, oxidation was nearly complete in 30 min., and complete after 3 hours and probably sooner. Although this process can be applied to as much as 50 g. it is not as satisfactory as other methods for the preparation of selenic and telluric acids.

